INFLUENCE OF EXCITATION FREQUENCY, TEMPERATURE AND HYDROGEN DILUTION ON THE STABILITY OF PECVD-DEPOSITED a-Si:H

R. Platz and S. Wagner

Department of Electrical Engineering, Princeton University, Olden Street, Princeton NJ 08544, USA

C. Hof and A. Shah

Institut de Microtechnique, Université de Neuchâtel, Rue A.-L. Breguet 2, CH-2000 Neuchâtel, Switzerland

S. Wieder and B. Rech

Institut für Schicht- und Ionentechnik - PV, Forschungszentrum Jülich, D-52425 Jülich, Germany

ABSTRACT

The first comparative study of DC, RF and VHF excitation for the plasma enhanced chemical vapor deposition (PECVD) of intrinsic layers of hydrogenated amorphous silicon (a-Si:H) is presented. The effects of hydrogen dilution on film stability are emphasized. Growth rates at comparable plasma power are presented for substrate temperatures between 100°C and 300°C and for various H_2 dilution ratios. The optical bandgap, H content, and electronic transport properties in the light-soaked state were measured.

H_2 dilution strongly reduces the growth rate for all techniques. The growth rate for the highest H_2 dilution ratio is higher for VHF (~4 Å/s) than for DC (~3 Å/s) or RF (0.5-1 Å/s) excitation. In all three cases increasing the substrate temperature reduces the optical gap and the H content C_H. Raising the substrate temperature slightly enhances stability. H_2 dilution increases the optical gap for all three techniques. The H content of RF- and VHF-deposited samples increases with increasing H_2 dilution ratio, while in DC deposition it produces an initial drop of the H content, followed by an increase.

In all three cases, H_2 dilution improves the electronic transport properties of the material by roughly a factor of two. The gain in stability is most pronounced for relatively small dilution; in the case of DC deposition, too strong a dilution even has an adverse effect on stability.

We rule out universal relation between hydrogen content of the a-Si:H films and their stability against light-soaking. Enhanced stability may be obtained for films which incorporate either more or less hydrogen than standard a-Si:H.

I. INTRODUCTION

Since the first observation of enhanced stability of a-Si:H films deposited with H_2 dilution [1] this technique has become the only tool available at the production level proven to result in a-Si:H solar cells with improved stability against light-soaking. However, the proper choice of plasma excitation frequency in combination with H_2 dilution has not yet been resolved satisfactorily.

In the present paper, we directly compare standard radio frequency (RF, 13.56 MHz) deposition to very high frequency (VHF) deposition at 70 MHz and deposition using a direct current (DC) excitation, all with special emphasis on the influence of H_2 dilution. All three methods have shown potential for producing solar cells with high stabilized efficiency (e.g., [2,3] for RF, [4] for VHF and [5] for DC).

II. EXPERIMENTS

Three different deposition systems were used for the deposition of the a-Si:H films. Each of the three systems was built and optimized for a given excitation frequency. The DC-deposited films were made in the i-chamber of a three-chamber PECVD system with load-lock at Princeton. We also deposited a few layers using RF-excitation in this reactor (referred to as RF(P)). All other intrinsic layers using RF-excitation were deposited in the i-chamber of a three-chamber system with load-lock at Jülich. Depositions using the VHF excitation technique at 70 MHz were performed in a load-locked single chamber reactor at Neuchâtel, designed especially for the VHF-GD technique. Table 1 gives an overview of the deposition conditions used for the three techniques.

The temperatures given throughout this work are true substrate temperatures, determined by calibration for conditions corresponding to those during deposition. The plasma excitation power was chosen to be comparable in all three cases. For the DC-deposited films, the plasma burns towards both sides of the powered electrode, due to the triode-configuration of the reactor. The effective electrode

surface is therefore doubled. The value of 44 mW/cm^2 given in the table is the value of the input power divided by the single electrode surface. The input power given for RF and VHF deposition was measured by a power meter between the generator and the matching network, and the value for DC deposition is given by current and voltage of the discharge.

Corning 7059 glass, and crystalline silicon substrates for infrared (IR) spectroscopy, were used in parallel for all depositions.

The optical absorption coefficient was measured by transmission, and C_H by integration of the 640 cm^{-1} absorption peak in the IR absorption spectrum, using

$$C_H[\text{at.\%}] = \frac{2.1\cdot 10^{19}\,\text{cm}^{-2}}{5\cdot 10^{22}\,\text{cm}^{-3}} \int \frac{\alpha(\omega)}{\omega} d\omega .$$

DC- and VHF-deposited films were degraded to saturation by a combination of pulsed dye laser degradation and HeNe laser illumination [6]. The transport properties were characterized using the mobility-lifetime product $\mu_0\tau_0$, which combines information on the majority carriers (from photo-conductivity (σ_{ph}) measurements) and the minority carriers (from the steady-state photo-carrier grating, SSPG, technique) [7]:

$$\mu_0\tau_0 = \frac{\sigma_{ph}}{eG}\cdot\frac{1}{z} ,$$

where G is the generation ratio, e the elementary charge and the correction factor z is defined as

$$z = \frac{p_f}{n_f}\cdot\frac{\sigma_p^0}{\sigma_n^+} + 1 + \frac{n_f}{p_f}\cdot\frac{\sigma_n^0}{\sigma_p^-} ,$$

n_f and p_f being the density of free electrons and holes, respectively, and σ the capture cross sections of the dangling bonds.

$\mu_0\tau_0$ correlates with the performance of a-Si:H p-i-n solar cells [7,8]. RF-deposited films were light-soaked for 600 h using 100 mW/cm^2 white light and characterized by photo-conductivity and constant photo-current method (CPM) measurements [3].

III. GROWTH RATE

The growth rate of the a-Si:H films is plotted in Figure 1 as a function of the H_2 dilution ratio (=$[H_2]/[SiH_4]$) for the three excitation techniques and a substrate temperature of ~200ºC. For undiluted films, VHF deposition yields the highest growth rate of over 4 Å/s; however, the growth rate obtained with DC excitation is only slightly lower. The growth rate of RF-deposited films without H_2 dilution is ~2 Å/s. The influence of H_2 dilution is quite different for the three excitation frequencies. We observe a roughly linear dependence of the growth rate on the H_2 dilution ratio in the case of VHF excitation. The range of H_2 dilution is very limited for the VHF technique as microcrystalline growth starts already at a dilution ratio of ~12. Above 200ºC microcrystalline growth sets in at even lower H_2 dilution ratios. The RF growth rate is lower and also almost linear with H_2 dilution. The RF growth rate drops by almost a factor of two between pure SiH_4 and dilution ratio of one. Microcrystalline growth sets in at dilution ratios exceeding 30. The growth rate of the DC-deposited films drops by a factor of three between H_2 dilution ratios of zero and eight, almost parallel to VHF deposition. More H_2 in the plasma reduces the growth rate further, but with a smaller slope and similar to RF deposition. We observe the onset of microcrystalline growth at 190ºC for H_2 dilution ratios of ≤30. We conclude that VHF clearly favors microcrystalline growth, which starts at very low H_2 dilution ratios. DC and RF deposition both require much higher H_2 dilution ratios to yield microcrystals. The amount of H_2 dilution to obtain microcrystalline films appears lower for DC than for RF excitation.

IV. OPTICAL GAP AND HYDROGEN CONTENT

4.1. Influence of the substrate temperature

In all three cases the substrate temperature has a relatively small influence on the growth rate. The growth rate increases slightly with increasing substrate temperature and at any temperature follows the

same dependence on the H_2 dilution ratio as plotted in Figure 1. The optical gap and the material properties of the a-Si:H films, in contrast, are strongly influenced by the substrate temperature. We varied the substrate temperature between ~100°C and ~300°C. The optical gap of intrinsic a-Si:H films deposited without H_2 dilution decreases with increasing substrate temperature. This decrease is an approximately linear function of the substrate temperature for all three excitation frequencies in the temperature range investigated (Figure 2a) with a slope of approximately –55 meV/100 K.

The decrease in the optical gap of the a-Si:H films correlates with a decrease in the H content (C_H) in the films as determined from FTIR spectroscopy (Figure 2b). Again, for all three excitation techniques, C_H is an approximately linear function of the substrate temperature in the investigated temperature range (-4.3 at.%/100 K). All excitation frequencies yield comparable values for the optical gap and the hydrogen content. The optical gap is therefore also an approximately line function of the hydrogen content in the film with $dE_{04}/dC_H \sim 12$ meV/at.%.

4.2. Influence of hydrogen dilution

The influence of H_2 dilution depends on the excitation frequency. In all three cases, the optical gap E_{04} increases with H_2 dilution (Figure 3a). For VHF and RF excitation techniques, the increase is monotonic and almost linear. In the case of RF excitation, a H_2 dilution ratio of 30 results in approximately the same increase in E_{04} as a dilution of ten for VHF (~0.05-0.1 eV). For all H_2 dilution ratios (and temperatures, cf. Figure 2a) the absolute values of the optical gap are higher for the VHF deposition technique than for RF deposition.

DC deposition exhibits a different response to H_2 dilution. For low H_2 dilution ratios, the optical gap increases moderately and similarly to VHF. Between a dilution ratio of four and six, however, the increase in the optical gap is very steep, followed by an increase to >2.05 eV with further dilution. Sub-

bandgap absorption spectra and UV reflectance measurements [9] indicate that these samples still are purely amorphous.

The H content of the RF and VHF films increases with increasing H_2 dilution ratio (Figure 3b). The increase in C_H is much more pronounced for the VHF than for the RF samples, and C_H exceeds 20 at.% for the highest dilution. However, we find again for both, RF- and VHF-deposited samples, a correlation between the optical gap and the H content.

The DC samples exhibit an anomaly in the influence of H_2 dilution on the H content. The optical gap increases with H_2 dilution, though not monotonically. The H content, in contrast, initially decreases and reaches a minimum at a H_2 dilution ratio of ~4. For still higher H_2 dilution ratios the H content increases as it does for VHF and RF deposition. In this case hydrogen content and optical gap are not directly correlated. In fact, despite the decrease in H content the optical gap increases for small H_2 dilution ratios. Our DC data are in contrast to the common observation that the optical gap correlates with the hydrogen content. [e.g., 10,11]. We also observe this common correlation when varying the deposition temperature (Figure 2). Bennett et al. [12] also reported a decrease in the H content and a moderately increased optical gap for DC samples deposited with H_2 dilution ratios of up to ten. It has been suggested [13] that the optical gap is determined by the degree of disorder in the lattice rather than the H content.

V. TRANSPORT PROPERTIES AND STABILITY

The primary goal of H_2 dilution is to enhance the stability of a-Si:H against light-induced degradation.

Figure 4 shows the $\mu_0\tau_0$ product in the degraded state for VHF-deposited samples as a function of the H_2 dilution ratio for deposition temperatures between 195°C and 280°C. The $\mu_0\tau_0$ product for

samples deposited without H_2 dilution improves slightly with increasing substrate temperature, and considerably with H_2 dilution. A H_2 dilution ratio of two raises $\mu_0\tau_0$ by a factor of two. A further increase in the H_2 dilution ratio does not raise $\mu_0\tau_0$, whereas the optical gap continues to increase.

In RF-deposited films (Figure 5), higher deposition temperatures similarly result in higher photo-conductivity and lower defect density in the degraded state for films deposited without H_2 dilution. H_2 dilution also raises σ_{ph} and reduces the defect density, both by up to a factor of 2-3. The material quality continuously increases with increasing H_2 dilution, even though most of the improvement is achieved already for a H_2 dilution ratio of ten.

Likewise, the $\mu_0\tau_0$ product in the DC films improves with increasing substrate temperature (Figure 6). H_2 dilution has a beneficial effect at low dilution ratios: the degraded $\mu_0\tau_0$ product is roughly a factor of two higher for samples deposited with a dilution ratio of 2-4 than for undiluted films, which is comparable to the improvement achieved for VHF-deposited samples (Figure 4). For high dilution ratios, in contrast to the observations for VHF and RF deposition, the quality of the films decreases again, even to below the value for undiluted films. It is interesting to note that maximum stability correlates with minimum hydrogen content (Figure 3b). In the case of DC excitation, material with enhanced stability thus is equivalent to material containing less hydrogen, similar to what is observed when the substrate temperature is varied (Figure 7). In contrast, for RF and VHF deposition with H_2 dilution the stability is enhanced in material containing more hydrogen than material deposited without H_2 dilution.

VI. DISCUSSION

H_2 dilution enhances the electronic quality of a-Si:H in the light-soaked state for all the investigated excitation methods. For the DC deposition technique we observe an optimum H_2 dilution ratio whereas

VHF and RF exhibit a pronounced improvement for small H_2 dilutions followed by a rather small additional effect for still higher H_2 dilution ratios. For application as an intrinsic layer in a-Si:H solar cells, the stability of the material is only one issue. All three excitation techniques result in a more or less pronounced increase in the optical gap of a-Si:H deposited with H_2 dilution. This in turn requires thicker i-layers to obtain a given current density, thus affecting the stability of the device. However, this effect is an advantage for the thin a-Si:H top cells in tandem or triple junctions. For these wide-gap cells the necessary thickness adjustment is generally small, resulting in an overall efficiency gain from the enhanced stability coupled with the higher V_{oc} that results from the higher optical gap of the i-layer. In other applications, such as in the top cell of a micromorph tandem cell [14] the increase in the optical gap due to H_2 dilution is unwanted and undiluted i-layers are required [15].

The reduced growth rate under H_2 dilution may become an important issue in industrial production. For VHF deposition we observe the best stabilized electronic properties for a H_2 dilution ratio of two (~4 Å/s). DC deposition yields comparable values for the degraded $\mu_0\tau_0$ product for a H_2 dilution ratio of four (~2.9 Å/s). RF deposition yields considerably lower growth rates (~1 Å/s at a H_2 dilution ratio of ten and ~0.5 Å/s at a dilution of 30). Therefore, as intrinsic a-Si:H material of more or less equal quality can be obtained by all three deposition techniques, the growth rate may become the decisive factor for the choice of excitation frequency.

An intriguing question is the correlation between hydrogen content of the a-Si:H films and their stability against light-soaking. Here we have shown that films of enhanced stability against light-soaking can be obtained by different means:

Deposition at high substrate temperature results in significant improvement of the electronic transport properties in the degraded state (Figure 7). For all three deposition techniques, DC, RF, and VHF, we observe a decrease in the H content for films deposited at high temperature (Figure 2b). This

observation is in agreement with the results obtained for the hot wire (HW) deposition technique [16,17]. HW films also appear to derive their enhanced stability against light-soaking from a low hydrogen content [18-22]. These observations raise the question to which extent the enhanced stability of HW-deposited films is produced by the high deposition temperature (at values extrapolated to higher temperatures in Figure 7), and to which extent by a specific hot wire or structural effect [23].

Deposition using the hydrogen dilution method also enhances the stability of a-Si:H films. However with H_2 dilution the enhanced stability indeed correlates with increased H content, in the RF- and VHF-deposited samples. DC-deposited samples also exhibit improved stability when deposited with H_2 dilution, but in their case the more stable films contain less hydrogen than standard undiluted films. The following Table 2 illustrates this paradox:

Therefore, no unique relation does exist between the hydrogen content of a-Si:H films and their stability against light-soaking.

CONCLUSIONS

Hydrogen dilution is a well-suited tool to all three excitation techniques, DC, RF and VHF, for obtaining a-Si:H with improved stability. H_2 dilution results in an increase in the optical gap for all three techniques. The hydrogen content of RF- and VHF-deposited samples increases with increasing H_2 dilution ratio. DC deposition with increasing H_2 dilution first lowers and then raises the hydrogen content. Raising the substrate temperature in all three cases reduces the optical gap and the H content. The stability of samples deposited at higher substrate temperature from undiluted SiH_4 is slightly enhanced. No unique relation does exist between hydrogen content and stability against light-soaking.

In all three cases of excitation, the electronic quality of light-soaked material is improved by roughly a factor of two upon H_2 dilution. Optimum H_2 dilution ratios are ~4 for DC, 10-30 for RF and ~2 for

VHF excitation. H_2 dilution strongly reduces the growth rate for all techniques. The growth rate for the best VHF-deposited material is ~4 Å/s, which is 35 % higher than for the equivalent DC-deposited sample (2.9 Å/s), and 4-8 times the value for the best RF-deposited film (0.5-1 Å/s).

ACKNOWLEDGEMENTS

R. Platz thanks the Arthur u. Aenne Feindt Stiftung, Hamburg (Germany), the Fondation Charles-Edouard Guillaume, Bienne (Switzerland), and the Electric Power Research Institute for providing support for his stay at Princeton University. The authors thank S. Dubail for his technical assistance, as well as C. Beneking and F. Siebke for helpful discussions.

TABLES AND FIGURES

	Electrode dimensions	Electrode area [cm^2]	El.-substr. distance [cm]	Pressure undiluted films [mbar]	Pressure diluted films [mbar]	Power density [mW/cm^2]
DC	15×15 cm^2	225	1.6	0.67	0.93	44 (×1/2)
RF	∅ 13.5 cm	143	1.2	1.33	2.66	30
RF(P)	15×15 cm^2	225	1.6	0.67	-	22
VHF	∅ 13.0 cm	133	1.6	0.35	0.5	30

Table 1

	increased T_s - hydrogen content	H_2 dilution - hydrogen content
DC	reduced	reduced
RF	reduced	increased
VHF	reduced	increased
HW	reduced [e.g., 16,17]	

Table 2

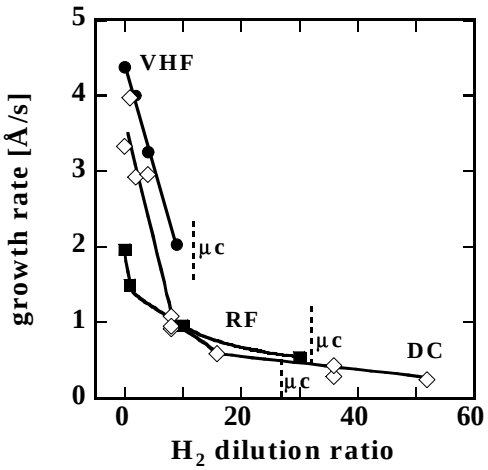
growth rate [Å/s]
5
4
3
2
1
0
VHF
µc
RF
µc
µc
DC
0
20
40
60
H2 dilution ratio

Figure 1

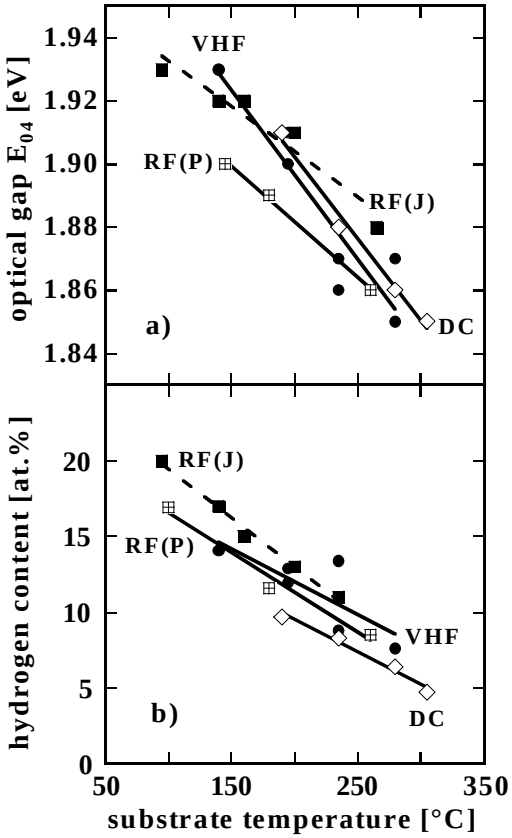
optical gap E_{04} [eV]
1.94
1.92
1.90
1.88
1.86
1.84
VHF
RF(P)
RF(J)
DC
a)
hydrogen content [at.%]
20
15
10
5
0
RF(J)
RF(P)
VHF
DC
b)
50
150
250
350
substrate temperature [°C]

Figure 2

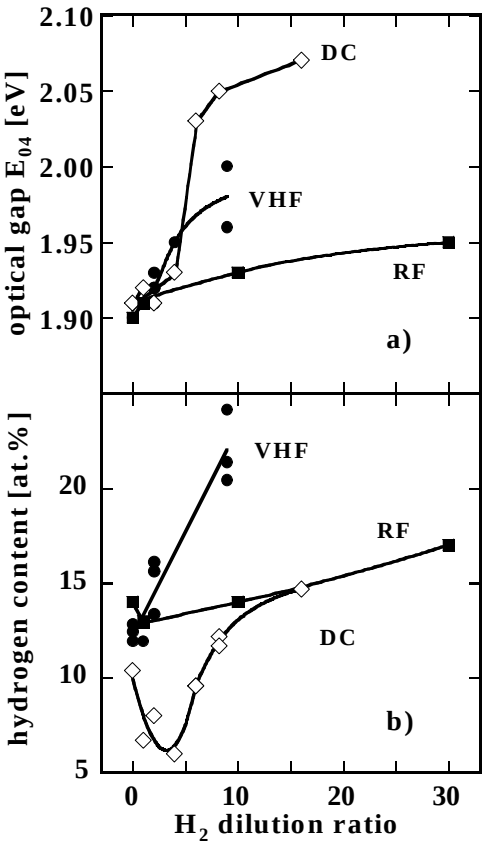
2.10
2.05
2.00
1.95
1.90
optical gap E_{04} [eV]
DC
VHF
RF
a)
hydrogen content [at.%]
20
15
10
5
VHF
RF
DC
b)
0
10
20
30
H_2 dilution ratio

Figure 3

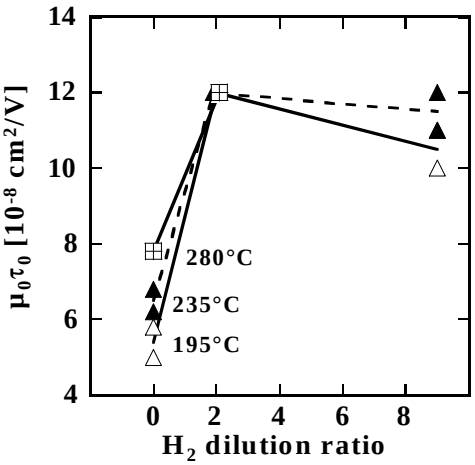
14
12
10
8
6
4
0
2
4
6
8
$\mu_0\tau_0$ [10^{-8} cm^2/V]
H_2 dilution ratio
280°C
235°C
195°C

Figure 4

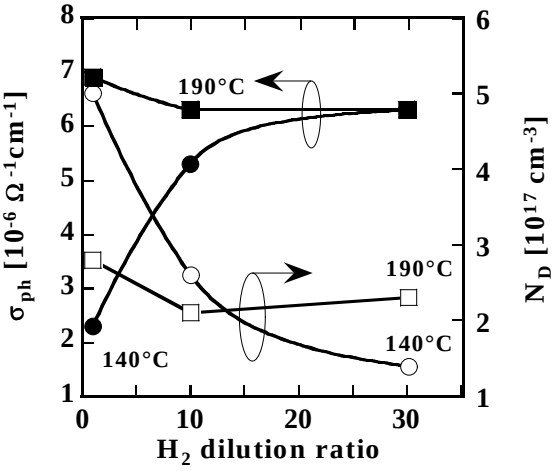
190°C
190°C
140°C
140°C
σph [10-6 Ω-1cm-1]
ND [1017 cm-3]
H2 dilution ratio
0
10
20
30
1
2
3
4
5
6
7
8

Figure 5

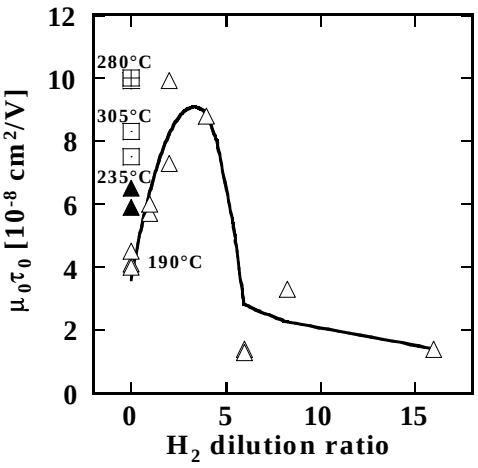
12
10
8
6
4
2
0
0
5
10
15
280°C
305°C
235°C
190°C
$\mu_0\tau_0$ [10^{-8} cm^2/V]
H_2 dilution ratio

Figure 6

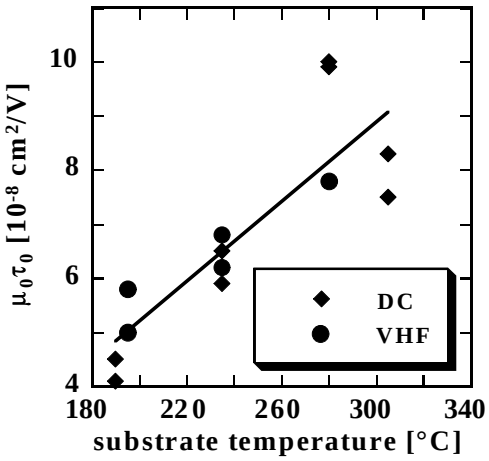
10
8
6
4
180
220
260
300
340
substrate temperature [°C]
μ0τ0 [10-8 cm2/V]
DC
VHF

Figure 7

FIGURE CAPTIONS

Table 1: Geometrical dimensions of the electrodes, and deposition conditions.

Table 2: Overview on the influence of different means to enhance the stability on the hydrogen content in the film for the different deposition techniques. 'Reduced' and 'increased' refers to a-Si:H deposited at standard temperature (~200ºC) without H_2 dilution.

Figure 1: Growth rate for VHF, RF and DC deposition as a function of the H_2 dilution ratio (=$[H_2]/[SiH_4]$). Input power is 30 mW/cm^2 (VHF), 30 mW/cm^2 (RF) and 44 mW/cm^2 (DC). T_s ~200°C.

Figure 2a): Optical gap E_{04} as a function of the deposition temperature for films deposited without H_2 dilution and VHF, RF (Jülich and Princeton) or DC excitation.
b): Hydrogen content as a function of the deposition temperature for films deposited without H_2 dilution by VHF, RF or DC excitation.

Figure 3a): Optical gap E_{04} for VHF, RF and DC deposition at a substrate temperature ~200ºC as a function of the H_2 dilution ratio of the plasma. All samples in the figure are purely amorphous.
b): Hydrogen content for VHF, RF and DC deposited samples as a function of the H_2 dilution ratio.

Figure 4: $\mu_0\tau_0$ product in the degraded state for VHF-deposited films as a function of the H_2 dilution ratio.

Figure 5: Defect density and photo-conductivity values in the degraded state for RF-deposited films as a function of the H_2 dilution ratio.

Figure 6: $\mu_0\tau_0$ product in the degraded state for DC-deposited films as a function of the H_2 dilution ratio.

Figure 7: $\mu_0\tau_0$ product in the degraded state for DC- and VHF-deposited films as a function of the deposition temperature.

REFERENCES

1 S. Guha, K.L. Narasimhan and S.M. Pietruszko, J. Appl. Phys. 52 (1981) 859.

2 S. Guha, Proc. 25th IEEE PVSC (1996) 1017.

3 B. Rech, S. Wieder, F. Siebke, C. Beneking, H. Wagner, MRS Symp. Proc. 420 (1996) 33.

4 R. Platz, D. Fischer, S. Dubail and A. Shah, Solar Energy Materials and Solar Cells 46 (1997) 157.

5 L. Yang, M. Bennett, L. Chen, K. Jansen, J. Kessler, Y. Li, J. Newtown, K. Rajan, F. Willing, R. Arya, D. Carlson, MRS Symp. Proc. 420 (1996) 839.

6 C. Hof, Y. Ziegler, R. Platz, N. Wyrsch and A. Shah, Proc. ICAMS-7 (Budapest 1997), in print.

7 N. Beck, N. Wyrsch, C. Hof and A. Shah, J. Appl. Phys. 79 (1996) 9361.

8 C. Hof, N. Beck, N. Wyrsch, D. Fischer, A. Shah, Proc. 13th European PVSEC (1995) 1634.

9 T.I. Kamins, Polycrystalline silicon for integrated circuit applications, Kluwer Academic Publishers 1988, p.68.

10 Y.S. Tsuo, E.B. Smith, S.K. Deb, Appl. Phys. Lett. 51 (1987) 1436.

11 N. Maley, J.S. Lannin, Phys. Rev. B36 (1987) 1146.

12 M. Bennett, K. Rajan, K. Kritikson, Proc. 23rd IEEE PVSC (1993) 845.

13 G.D. Cody, T. Tiedje, B. Abeles, B. Brooks, Y. Goldstein, Phys. Rev. Lett. 47 (1981) 1480.

14 R. Platz, J. Meier, D. Fischer, S. Dubail, A. Shah, MRS Symp. Proc. 467 (1997) 699.

15 R. Platz, C. Hof, D. Fischer, J. Meier, A. Shah, Solar Energy Materials and Solar Cells, in print.

16 H. Matsumura, J. Appl. Phys. 65 (1989) 4396.

17 A.H. Mahan, J. Carapella, B.P. Nelson, R.S. Crandall, I. Balber, J. Appl. Phys. 69 (1991) 6728.

18 M. Vanecek, A.H. Mahan, B.P. Nelson, R.S. Crandall, Proc. 11th European PVSEC (1993) 96.

19 D. Kwon, J.D. Cohen, B.P. Nelson, E. Iwaniczko, MRS Symp. Proc. 377 (1995) 301.

20 R. Zedlitz, F. Kessler, M. Heintze, J. Non-Cryst. Solids 164-166 (1993) 83.

21 P. Papapdopulos, A. Scholz, S. Bauer, B. Schröder, H. Oechsner, J. Non-Cryst. Solids 164-166 (1993) 87.

22 M. Vanecek, A.H. Mahan, B.P. Nelson, R.S. Crandall, Proc. 12th European PVSEC (1994) 354.

23 J.T. Stephen, D. Han, A.H. Mahan, Y. Wu, MRS Symp. Proc. 420 (1996) 485.